

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
REQUEST FOR FILING NATIONAL PHASE OF
PCT APPLICATION UNDER 35 U.S.C. 371 AND 37 CFR 1.494 OR 1.495

To: Hon. Commissioner of Patents
 Washington, D.C. 20231



00909

TRANSMITTAL LETTER TO THE UNITED STATES
 DESIGNATED/ELECTED OFFICE (DO/EO/US)

Atty Dkt: P 290579 /EUR 50799/USw
 M# /Client Ref.

From: Pillsbury Winthrop LLP, IP Group:

Date: January 10, 2002

This is a **REQUEST** for **FILING** a PCT/USA National Phase Application based on:

1. International Application	2. International Filing Date	3. Earliest Priority Date Claimed
<u>PCT/EP00/06057</u>	<u>29 June 2000</u>	<u>26 July 1999</u>
<u>↑ country code</u>	<u>Day MONTH Year</u>	<u>Day MONTH Year</u>
		(use item 2 if no earlier priority)

4. Measured from the earliest priority date in item 3, this PCT/USA National Phase Application Request is being filed within:

(a) ☐ 20 months from above item 3 date (b) ☒ 30 months from above item 3 date,

(c) Therefore, the due date (unextendable) is January 26, 2002

5. Title of Invention POLYISOCYANTE COMPOSITIONS FOR FAST CURE

6. Inventor(s) Christopher John SKINNER

Applicant herewith submits the following under 35 U.S.C. 371 to effect filing:

7. ☒ Please immediately start national examination procedures (35 U.S.C. 371 (f)).

8. ☐ A copy of the International Application as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (file if in English but, if in foreign language, file only if not transmitted to PTO by the International Bureau) including:

- a. ☐ Request;
 b. ☒ Abstract;
 c. 16 pgs. Spec. and Claims;
 d. sheet(s) Drawing which are ☐ informal ☐ formal of size ☐ A4 ☐ 11"

9. ☒ A copy of the International Application has been transmitted by the International Bureau.

10. A translation of the International Application into English (35 U.S.C. 371(c)(2))

- a. ☐ is transmitted herewith including: (1) ☐ Request; (2) ☐ Abstract;
 (3) pgs. Spec. and Claims;
 (4) sheet(s) Drawing which are:
 ☐ informal ☐ formal of size ☐ A4 ☐ 11"
- b. ☒ is not required, as the application was filed in English.
- c. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.
- d. ☐ Translation verification attached (not required now).

JC13 Rec'd PCT/PTO 10 JAN 2002

11. ☒ Please see the attached Preliminary Amendment
12. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., **before 18th month from first priority date above in item 3, are transmitted herewith (file only if in English) including:**
13. ☒ PCT Article 19 claim amendments (if any) have been transmitted by the International Bureau
14. ☐ Translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., of **claim amendments** made before 18th month, **is attached (required by 20th month from the date in item 3 if box 4(a) above is X'd, or 30th month if box 4(b) is X'd, or else amendments will be considered canceled).**

15. **A declaration of the inventor** (35 U.S.C. 371(c)(4))

- a. ☒ is submitted herewith ☒ Original ☐ Facsimile/Copy
- b. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.

16. **An International Search Report (ISR):**

- a. Was prepared by ☒ European Patent Office ☐ Japanese Patent Office ☐ Other
- b. ☒ has been transmitted by the international Bureau to PTO.
- c. ☐ copy herewith (___ pg(s).) ☐ plus Annex of family members (___ pg(s).).

17. **International Preliminary Examination Report (IPER):**

- a. ☒ has been transmitted (if this letter is filed after 28 months from date in item 3) in English by the International Bureau with Annexes (if any) in original language.
- b. ☐ copy herewith in English.
- c.1 ☐ IPER Annex(es) in original language ("Annexes" are amendments made to claims/spec/drawings during Examination) including attached amended:
- c.2 ☐ Specification/claim pages # ___ claims # ___
Dwg Sheets # ___
- d. ☐ Translation of Annex(es) to IPER **(required by 30th month due date, or else annexed amendments will be considered canceled).**

18. **Information Disclosure Statement** including:

- a. ☒ Attached Form PTO-1449 listing documents
- b. ☒ Attached copies of documents listed on Form PTO-1449
- c. ☒ A concise explanation of relevance of ISR references is given in the ISR.

19. ☒ **Assignment** document and Cover Sheet for recording are attached. Please mail the recorded assignment document back to the person whose signature, name and address appear at the end of this letter.
20. ☐ Copy of Power to IA agent.
21. ☐ **Drawings** (complete only if 8d or 10a(4) not completed): ___ sheet(s) per set: ☐ 1 set informal; ☐ Formal of size ☐ A4 ☐ 11"

22. Small Entity Status ☒ is **Not** claimed ☐ is claimed (**pre-filing confirmation required**)
- 22(a) ___ (No.) Small Entity Statement(s) enclosed (since 9/8/00 Small Entity Statements(s) not essential to make claim)

23. **Priority** is hereby claimed under 35 U.S.C. 119/365 based on the priority claim and the certified copy, both filed in the International Application during the international stage based on the filing in (country) EP of:

	Application No.	Filing Date		Application No.	Filing Date
(1)	99114601.0	July 26, 1999	(2)		
(3)			(4)		
(5)			(6)		

- a. ☒ See Form PCT/IB/304 sent to US/DO with copy of priority documents. If copy has not been received, please proceed promptly to obtain same from the IB.
- b. ☐ Copy of Form PCT/IB/304 attached.

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24. Attached:

25 Per Item 17.c2, cancel original pages # __, claims # __, Drawing Sheets #26. **Calculation of the U.S. National Fee (35 U.S.C. 371 (c)(1)) and other fees is as follows:**Based on amended claim(s) per above item(s) ☐ 12, ☐ 14, ☐ 17, ☐ 25 (hilite)

Total Effective Claims	23	minus 20 =	3	x \$18/\$9	=	\$54	966/967
Independent Claims	2	minus 3 =	0	x \$84/\$42	=	\$0	964/965
If any proper (ignore improper) Multiple Dependent claim is present,				add \$280/\$140	+	0	968/969

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(4)): →→ **BASIC FEE REQUIRED, NOW** →→→→A. If country code letters in item 1 are not "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"

See item 16 re:

1. Search Report was <u>not</u> prepared by EPO or JPO -----	add \$1,040/\$52	0	960/961
2. Search Report was prepared by EPO or JPO -----	add \$890/\$445	+890	970/971

SKIP B, C, D AND E UNLESS country code letters in item 1 are "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN", "ZA", "LC" or "PH"

→ <input type="checkbox"/> B. If USPTO did not issue both International Search Report (ISR) and (if box 4(b) above is X'd) the International Examination Report (IPER), -----	add \$1,040/\$52	+0	960/961
→ <input type="checkbox"/> C. If USPTO issued ISR but not IPER (or box 4(a) above is X'd), -----	add \$740/\$370	+0	958/959
→ <input type="checkbox"/> D. If USPTO issued IPER but IPER Sec. V boxes <u>not all</u> 3 YES, -----	add \$710/\$355	+0	956/957
→ <input type="checkbox"/> E. If international preliminary examination fee was paid to USPTO and Rules 492(a)(4) and 496(b) <u>satisfied</u> (in IPER Sec. V <u>all</u> 3 boxes <u>must</u> be YES for <u>all</u> claims), --	add \$100/\$50	+0	962/963
SUBTOTAL =		\$944	

28. If Assignment box 19 above is X'd, add Assignment Recording fee of ----\$40 +40 (581)

29. If box 15a is x'd, determine whether inventorship on Declaration is different than in international stage. If yes, add (per Rule 497(d)) ----\$130 + (098)

30. Attached is a check to cover the ----- **TOTAL FEES** **\$984**

Our Deposit Account No. 03-3975

Our Order No. 38266 290579
C# M#

00909

CHARGE STATEMENT: The Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or any missing or insufficient fee(s) filed, or asserted to be filed, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 and 492 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to our Account/Order Nos. shown above for which purpose a duplicate copy of this sheet is attached.

This CHARGE STATEMENT does not authorize charge of the issue fee until/unless an issue fee transmittal form is filedPillsbury Winthrop LLP
Intellectual Property GroupBy Atty: Richard A. SteinbergReg. No. 26588

Atty/Sec: RAS:cdw

Sig: Richard A. SteinbergFax: (703) 905-2500NOTE: File in duplicate with 2 postcard receipts (PAT-103) & attachments.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION of:

SKINNER

Group Art Unit: TBA

Application No.: TBA

Examiner: TBA

Filed: January 10, 2002

FOR: POLYISOCYANTE COMPOSITIONS FOR FAST CURE

* * * * *

January 10, 2002

PRELIMINARY AMENDMENT

Hon. Commissioner of Patents
Washington, D.C. 20231

Sir:

Prior to examination on the merits, please amend the above-identified patent in the manner set forth below.

IN THE SPECIFICATION:

At the top of the first page, just under the title, insert

--This application is the National Phase of International Application PCT/EP00/06057 filed June 29, 2000, which designated the U.S. and that International Application was published under PCT Article 21(2) in English. The PCT application is hereby incorporated in its entirety by reference. --

IN THE CLAIMS:

Please amend the claims as follows:

4. (Amended) A polyisocyanate composition according to claim 1 in which the acetoacetate ester is ethyl acetoacetate.

5. (Amended) A polyisocyanate composition according to claim 1 in which the complex has been prepared from a titanium alkoxide having the general formula $M(OR)_4$ in which M is Ti and R is substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group.

8. (Amended) A polyisocyanate composition according to claim 1 in which the complex has been prepared from a condensed titanium alkoxide having the general formula $RO[M(OR)_2O]_xR$ in which M is Ti and x is an integer and R is substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group.

10. (Amended) A polyisocyanate composition according claim 1 in which the complex is prepared from an alkoxide and displaced alcohol is removed.

11. (Amended) A polyisocyanate composition according to claim 1 in which the complex is present in an amount in the range 0.03 to 1% by weight based on the polyisocyanate.

13. (Amended) A polyisocyanate composition according to claim 1 in which the polyisocyanate is diphenylmethane diisocyanate or a mixture of methylene bridged polyphenyl polyisocyanates.

14. (Amended) A polyisocyanate composition according to claim 1 additionally comprising a diluent.

17. (Amended) A polyisocyanate composition according to claim 1 additionally comprising a formaldehyde condensate adhesive resin.

22. (Amended) A process according to claim 20 in which the polyisocyanate composition is applied in such an amount as to give a weight ratio of polyisocyanate to lignocellulosic material in the range 0.1:99.9 to 20:80.

REMARKS

After introduction of the amendment set forth above, claims 1-23 will be pending in the application of which claims 1 and 20 are independent. Claims 4, 5, 8, 10, 11, 13, 14, 17 and 22 have been amended to eliminate multiple dependency of the claims. Support for the above amendments can be found throughout the original application as filed. Applicants submit that no new matter has been introduced by the amendment.

Respectfully submitted,

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Enclosure: Appendix

APPENDIX

VERSION WITH MARKINGS SHOWING CHANGES MADE

IN THE CLAIMS:

The claims are amended as follows:

4. (Amended) A polyisocyanate composition according to [any one of the preceding claims] claim 1 in which the acetoacetate ester is ethyl acetoacetate.
5. (Amended) A polyisocyanate composition according to [any one of the preceding claims] claim 1 in which the complex has been prepared from a titanium alkoxide having the general formula $M(OR)_4$ in which M is Ti and R is substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group.
8. (Amended) A polyisocyanate composition according to [any one of claims 1-7] claim 1 in which the complex has been prepared from a condensed titanium alkoxide having the general formula $RO[M(OR)_2O]_xR$ in which M is [Ti] Ti and x is an integer and R is substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group.
10. (Amended) A polyisocyanate composition according to [any one of the preceding claims] claim 1 in which the complex is prepared from an alkoxide and displaced alcohol is removed.
11. (Amended) A polyisocyanate composition according to [any one of the preceding claims] claim 1 in which the complex is present in an amount in the range 0.03 to 1% by weight based on the polyisocyanate.
13. (Amended) A polyisocyanate composition according to [any one of the preceding claims] claim 1 in which the polyisocyanate is diphenylmethane diisocyanate or a mixture of methylene bridged polyphenyl polyisocyanates.

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14. (Amended) A polyisocyanate composition according to [any one of the preceding claims] claim 1 additionally comprising a diluent.

17. (Amended) A polyisocyanate composition according to [any one of the preceding claims] claim 1 additionally comprising a formaldehyde condensate adhesive resin.

22. (Amended) A process according to claim 20 [or 21] in which the polyisocyanate composition is applied in such an amount as to give a weight ratio of polyisocyanate to lignocellulosic material in the range 0.1:99.9 to 20:80.

POLYISOCYANATE COMPOSITIONS FOR FAST CURE

This invention relates to polyisocyanate compositions and, in particular, to polyisocyanate compositions containing certain organometallic compositions based on Group IVB metals and which utility in accelerating the binding of the lignocellulosic material used in the manufacture of waferboard (known extensively as oriented strand board), medium density fiberboard and particle board (also known as chipboard).

The use of organic polyisocyanates as binders for lignocellulosic material in the manufacture of sheets or moulded bodies such as waferboard, chipboard, fibreboard and plywood is well known. In a typical process the organic polyisocyanate, optionally in the form of a solution, dispersion or aqueous emulsion, is applied to the lignocellulosic material which is then subjected to heat and pressure.

It has now been surprisingly found that specific Titanium compositions enhance the cure rate of binders such as starch, isocyanates when used for binding lignocellulosic materials especially oriented strand board

Furthermore It has been surprisingly found that certain polyisocyanate compositions containing certain compounds of Group IVB metals and acetoacetate esters are very stable on prolonged storage and provide significant acceleration to the binding of lignocellulosic material used in the core layers of waferboard (known extensively as oriented strand board), medium density fiberboard and particleboard while maintaining excellent physical properties.

According to the invention, a polyisocyanate composition comprising a titanium composition in which the molar ratio of Ti to acetoacetate ester is in the range 1 : 2.0 to 1:8 and said acetoacetate ester is an ester of an alcohol containing 1 to 4 carbon atoms.

The titanium composition used in the polyisocyanate composition of the invention is described herein as a "complex". It is believed that some of the acetoacetate ester will be chemically bound to the metal (Ti) but some can be described as "free" ester. The exact proportions which are bound and free will depend partly upon the exact molar ratios present in the complex but it has been shown that the "free" ester does influence the properties, particularly the stability on storage, of the polyisocyanate composition as a binder for lignocellulosic materials. The use of the word "complex" does not imply that said complex is necessarily separately prepared before addition to a polyisocyanate to form the compositions of the invention. The complex can be formed by preparing the inventive composition using several alternative methods as described hereinafter.

The molar ratio of titanium to acetoacetate ester in the complex is in the range 1 : 2.0 to 1 : 8. Preferably, in the range of 1 : 2.0 to 1 : 6 and more preferably in the range 1 : 2.5 to 1 : 5. In agreement with conventional theories about the co-ordination chemistry of titanium, it is believed that two molecules of acetoacetate ester will be chemically bound to a titanium atom and the remainder will be "free".

The preferred acetoacetate ester for preparing the complex is ethyl acetoacetate. The complex can be prepared from more than one acetoacetate ester but preferably only one acetoacetate ester is present in the complex.

Typically, the complex of titanium is prepared from a titanium alkoxide having the general formula $M(OR)_4$ in which M is Ti and R is a substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group. Preferably, R contains up to 6 carbon atoms and, more preferably, up to 4 carbon atoms. Generally, all four OR groups will be identical but alkoxides derived from a mixture of alcohols can be used and mixtures of alkoxides can be employed when more than one metal is present in the complex. Suitable alkoxides include tetramethoxytitanium, tetra-ethoxytitanium, tetra-isopropoxytitanium, tetra-n-

propoxytitanium, tetrabutoxytitanium, tetrakis(2-ethylhexoxy)titanium, tetrakis(2-ethoxyethoxy)-titanium.

Alternatively, the complex can be prepared from condensed alkoxides of titanium. These compounds can be represented by the general formula $RO[M(OR)_2O]_xR$, wherein
5 M and R have the same meaning as discussed above and x is an integer. Generally, these condensed alkoxides consist of a mixture containing compounds of the above formula with x having a range of values. Preferably, x has an average value in the range 2 to 16 and, more preferably, in the range 2 to 8. A condensed alkoxide is usually prepared by the controlled addition of water to an alkoxide, followed by removal of alcohol which is
10 displaced. Suitable condensed alkoxides include the compounds known as polybutyl titanate and polyisopropyl titanate. Complexes of condensed alkoxides can also be prepared by forming a complex of an acetoacetate ester with an alkoxide, adding water to the complex and removing any by-product alcohol.

Other titanium compounds, such as titanium tetrachloride or alkoxides which have
15 been substituted with, for example, glycol or phosphorus substituents can be used as raw materials for the formation of the complex used in the invention.

The complex can be readily prepared by mixing, for example, an alkoxide or condensed alkoxide with an appropriate amount of acetoacetate ester. Alcohol from the alkoxide will be displaced by the acetoacetate ester and, preferably, the displaced alcohol
20 is removed by, for example, distillation. In a preferred method, 2 moles of acetoacetate ester per atom of Ti are added to an alkoxide or condensed alkoxide and the displaced alcohol is removed by distillation. Any additional acetoacetate ester required is then added to the stripped product. This method is advantageous because it provides a consistent product of known stoichiometry. It is possible to add all the acetoacetate ester in one
25 charge and subsequently remove all the displaced alcohol but some of the "free"

acetoacetate ester is usually accidentally removed during this process, leading to inconsistent products and contamination of the displaced alcohol.

Alternatively, a product containing, for example, 2 moles of acetoacetate ester per Ti can be prepared according to the method outlined above and this can be mixed with a polyisocyanate. Any additional acetoacetate ester required to produce the polyisocyanate composition of the invention can be added to the polyisocyanate before or after the titanium-compound has been added. Other methods of preparing the composition of the invention will be apparent to a person skilled in this art.

The amount of titanium complex present in the polyisocyanate composition of the invention is usually in the range 0.01 to 5 % by weight, based on the polyisocyanate and, preferably, the amount is in the range 0.03 to 1 %. More preferably, the amount of complex present is in the range 0.05 to 0.5 % by weight with respect to polyisocyanate.

Polyisocyanates for use in the composition of the present invention may be any organic polyisocyanate compound or mixture of organic polyisocyanate compounds, provided said compounds have at least 2 isocyanate groups. Organic polyisocyanates include diisocyanates, particularly aromatic diisocyanates, and isocyanates of higher functionality.

Examples of organic polyisocyanates which may be used in the composition of the present invention include aliphatic isocyanates such as hexamethylene diisocyanate; and aromatic isocyanates such as m- and p-phenylene diisocyanate, tolylene-2,4- and tolylene-2,6-diisocyanate, diphenyl- methane-4,4'-diisocyanate, chlorophenylene-2,4-diisocyanate, naphthylene- 1,5-diisocyanate, diphenylene-4,4'-diisocyanate, 4,4'-diisocyanate- 3,3'-dimethyl-diphenyl, 3-methyldiphenylmethane-4,4'-diisocyanate and diphenyl ether diisocyanate; and cycloaliphatic diisocyanates such as cyclohexane-2,4- and -2,3-diisocyanate, 1-methylcyclohexyl-2,4- and -2,6-diisocyanate and mixtures thereof and bis-

(isocyanatocyclohexyl)methane and triisocyanates such as 2,4,6-triisocyanatotoluene and 2,4,4-triisocyanatodiphenylether.

Modified polyisocyanates containing isocyanurate, carbodiimide or uretonimine groups may be employed as well. Further blocked polyisocyanates, like the reaction
5 product of a phenol or an oxime and a polyisocyanate, may be used, having a deblocking temperature below the temperature applied when using the polyisocyanate composition.

The organic polyisocyanate may also be an isocyanate-ended prepolymer made by reacting an excess of a diisocyanate or higher functionality polyisocyanate with a polyol.

Water-emulsifiable organic polyisocyanates like those described in UK patent no. 1
10 444 933, in European patent publication no. 516 361 and in PCT patent publication no. 91/03082 can also be used.

Mixtures of isocyanates may be used, for example a mixture of tolylene diisocyanate isomers such as the commercially available mixtures of 2,4- and 2,6-isomers and also the mixture of di- and higher polyisocyanates produced by phosgenation of
15 aniline/formaldehyde condensates.

Such mixtures are well-known in the art and include the crude phosgenation products containing methylene bridged polyphenyl polyisocyanates, including diisocyanate, triisocyanate and higher polyisocyanates together with any phosgenation by-products.

20 Preferred isocyanates to be used in the present invention are those wherein the isocyanate is an aromatic diisocyanate or polyisocyanate of higher functionality such as a pure diphenylmethane diisocyanate or a mixture of methylene bridged polyphenyl polyisocyanates containing diisocyanates, triisocyanates and higher functionality polyisocyanates.

Methylene bridged polyphenyl polyisocyanates are well known in the art. They are prepared by phosgenation of corresponding mixtures of polyamines obtained by condensation of aniline and formaldehyde. For convenience, polymeric mixtures of methylene bridged polyphenyl polyisocyanates containing diisocyanate, triisocyanate and higher functionality polyisocyanates are referred to hereinafter as polymeric MDI. Suitable polyisocyanates include SUPRASECTM DNR, SUPRASECTM 2185, RUBINATETM M and RUBINATETM 1840, all available from Imperial Chemical Industries.

Preferably the polyisocyanate is liquid at room temperature.

In order to further improve the storage stability of the polyisocyanate composition of the present invention a diluent may be added to the composition. Suitable diluents include plasticizers of the type mentioned in "Taschenbuch der Kunststoff-Additive", Ed. by R. Gachter and H. Muller, Carl Hanser Verlag Munchen, third edition, 1989. Preferred diluents are phthalates, aliphatic carboxylates, fatty acid esters, linseed oil and soybean oil. These diluents are added in amounts of from 1 to 40 parts by weight per 100 parts by weight of polyisocyanate and preferably in amounts of from 1 to 15 parts by weight per 100 parts by weight of polyisocyanate.

The composition further may also comprise conventional additives like flame retardants, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, surfactants, thixotropic agents and other binders like formaldehyde condensate adhesive resins and lignin (optionally in combination with a lignin solvent such as described in PCT Patent Application No. EP96/00924).

The polyisocyanate composition of the present invention can be made by simply mixing the ingredients at room temperature.

The present invention is also concerned with a process for preparing lignocellulosic bodies by bringing lignocellulosic parts into contact with the present polyisocyanate composition and by pressing this combination.

Therefore the present invention also provides a process for binding lignocellulosic material comprising the steps of

- a) bringing said lignocellulosic material in contact with the present polyisocyanate composition and
- b) subsequently allowing said material to bind.

The lignocellulosic bodies are prepared by bringing the lignocellulosic parts into contact with the polyisocyanate composition by means such as mixing, spraying and/or spreading the composition with/onto the lignocellulosic parts and by pressing the combination of the polyisocyanate composition and the lignocellulosic parts, preferably by hot-pressing, normally at 140° C to 270° C and 2 to 6 MPa specific pressure.

Such binding processes are commonly known in the art.

In waferboard manufacture the lignocellulosic material and the polyisocyanate composition may be conveniently mixed by spraying the present polyisocyanate composition on the lignocellulosic material while it is being agitated.

The lignocellulosic material after treatment with the polyisocyanate composition is placed on caul plates made of aluminium or steel which serve to carry the furnish into the press where it is compressed to the desired extent usually at a temperature between 140° C and 270° C.

While the process is particularly suitable for the manufacture of waferboard known extensively as oriented strand board and will be largely used for such manufacture, the process may not be regarded as limited in this respect and can also be used in the

manufacture of medium density fiberboard, particle board (also known as chipboard) and plywood.

Thus the lignocellulosic material used can include wood strands, woodchips, wood fibres, shavings, veneers, wood wool, cork, bark, sawdust and like waste products of the wood working industry as well as other materials having a lignocellulosic basis such as paper, bagasse, straw, flax, sisal, hemp, rushes, reeds, rice hulls, husks, grass, nutshells and the like. Additionally, there may be mixed with the lignocellulosic materials other particulate or fibrous materials such as ground foam waste (for example, ground polyurethane foam waste), mineral fillers, glass fibre, mica, rubber, textile waste such as plastic fibres and fabrics.

When the polyisocyanate composition is applied to the lignocellulosic material, the weight ratio of polyisocyanate/lignocellulosic material will vary depending on the bulk density of the lignocellulosic material employed. Therefore, the polyisocyanate compositions may be applied in such amounts to give a weight ratio of polyisocyanate/lignocellulosic material in the range of 0.1 : 99.9 to 20 : 80 and preferably in the range of 0.5 : 99.5 to 10 : 90.

The polyisocyanate compositions of the present invention allows operating temperatures far below the standard operating temperatures. Hence major energy savings can be made.

If desired, other conventional binding agents, such as formaldehyde condensate adhesive resins, may be used in conjunction with the polyisocyanate composition.

More detailed descriptions of methods of manufacturing waferboard and similar products based on lignocellulosic material are available in the prior art. The techniques and equipment conventionally used can be adapted for use with the polyisocyanate compositions of the present invention.

The sheets and moulded bodies produced from the polyisocyanate compositions of the present invention have excellent mechanical properties and they may be used in any of the situations where such articles are customarily used.

5 The invention is illustrated but not limited by the following examples.

1000000-014000

EXAMPLE 1

A reactor was charged with tetraisopropyl titanate (1400kg, Tilcom® TIPT from ICI Vertec). Ethylacetoacetate (1282kg) was then added with stirring. The resulting product was a pale red liquid. The displaced alcohol (580 kg, isopropanol) was then removed by evaporation to leave a red liquid PRODUCT A (2090kg). This was then diluted by addition of ethylacetoacetate in the following molar ratio (1 mole PRODUCT A to 2.5M ethylacetoacetate) to yield PRODUCT B.

A polyisocyanate composition was then prepared comprising 0.18 parts weight of PRODUCT B described above and 100 parts by weight of standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) to yield a material PRODUCT C.

Stability testing of PRODUCT C vs Standard Isocyanate (Comparative)

The stability of PRODUCT C was evaluated by storing PRODUCT C 45° C and then testing the viscosity of each system at 25° C using a Brookfield viscometer at various time. The following data was obtained:

Results are reported below in Pa s.

Days	PRODUCT C	Comparative
21	280	244

To evaluate the utility of PRODUCT C in accelerating the curing of the core layers of an OSB panel against a standard polyisocyanate composition used industrially within the core of an OSB panel PRODUCT C was used to bind the softwood strands used in the core layers in the following manner:

Panels containing Product C

3 Layer boards were prepared of 15 x 400 x 400 mm at a density 650 kg/m³. MUPF resin was used to bind the face layers (11% resin loading based on dry wood). PRODUCT C was used to bind the core layer (4% resin loading based on dry wood). Both

layers also contained a sizing wax emulsion (SPG 60 available from Condea Chemie) at 1 % loading (solid wax) based on dry wood. The pre-pressing moisture content was 11 % in the face layers and 6% in the core layer.

5 *Standard Isocyanate (comparative)*

3 Layer boards were prepared of 15 x 400 x 400 mm at a density 650 kg/m³. MUPF resin was used to bind the face layers (11% resin loading based on dry wood) and standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) used to bind the core layer (4% resin loading based on dry wood). Both layers also
10 contained a sizing wax emulsion (SPG 60 available from Condea Chemie) at 1 % loading (solid wax) based on dry wood. The pre-pressing moisture content was again 11 % in the face layers and 6% in the core layer.

To determine the minimum cycle time a press temperature of 190^o C was used. The minimum possible cycle time was obtained by reducing the overall cycle time until a
15 failure in panel performance was evident (either through a loss of control over panel thickness or through adhesive failure). The following results were obtained for panels prepared as described earlier:

	Standard Polyisocyanate	PRODUCT C
Minimum cook time (seconds of pressing per mm of panel thickness)	7.0	6.3

20

The composite produced under conditions described above were then tested using a range of industry standard tests to measure physical properties (Modulus of elasticity and rupture according to EN310 / V100 internal bond according to EN1087 / Swelling after 24hrs of soaking in water according to EN317). The measured properties showed no significant
25 performance difference between composites prepared with SUPRASEC DNR and PRODUCT C and demonstrates the advantages of using polyisocyanate compositions of the invention to achieve accelerated binding of lignocellulosics relative to standard polyisocyanate compositions whilst not affecting physical performance of the resulting composite panels.

EXAMPLE 2

A polyisocyanate composition was prepared comprising 0.18 parts by weight of PRODUCT B (described above) and 100 parts by weight of standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) to yield a material
5 PRODUCT D.

To evaluate the utility of PRODUCT D in accelerating the curing of a OSB panel against a standard polyisocyanate composition used industrially within the core of an OSB panel PRODUCT D was then used to bind softwood strands in the following manner:

10 *Panels containing Product D*

3 Layer boards were prepared of 25 x 250 x 250 mm at a density 650 kg/m³. Standard polyisocyanate resin (SUPRASEC DNR, available from Imperial Chemical Industries) was used to bind the face layers (4% resin loading based on dry wood). PRODUCT D was used to bind the core layer (4% resin loading based on dry wood). Both
15 layers also contained a sizing wax emulsion (SPG 60 available from Condea Chemie) at 1 % loading (solid wax) based on dry wood. The prepressing moisture content was 11 % in the face layers and 6% in the core layer.

Standard Isocyanate

20 3 Layer boards were prepared of 25 x 250 x 250 mm at a density 650 kg/m³. Standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) resin was used to bind the face layers (4% resin loading based on dry wood) and standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) used to bind the core layer (4% resin loading based on dry wood). Both layers also contained a
25 sizing wax emulsion (SPG 60 available from Condea Chemie) at 1 % loading (solid wax) based on dry wood. The prepressing moisture content was again 11 % in the face layers and 6% in the core layer.

To determine the minimum cycle time a press temperature of 190° C was used. The minimum possible cycle time was obtained by reducing the overall cycle time until a
30 failure in panel performance was evident (either through a loss of control over panel thickness or through adhesive failure). The following results were obtained for panels prepared as described earlier:

	Standard Polyisocyanate	PRODUCT D
Minimum cook time (seconds of pressing per mm of panel thickness)	13.0	11.0

The above clearly demonstrates the advantages of using polyisocyanate compositions of the invention to achieve accelerated binding of lignocellulosics relative to standard polyisocyanate compositions whilst not affecting physical performance of the resulting composite panels.

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CLAIMS

1. A polyisocyanate composition comprising a titanium complex consisting of titanium and an acetoacetate ester in which the molar ratio of Ti to acetoacetate ester is in the range 1: 2 to 1:8 and said acetoacetate ester is an ester of an alcohol containing 1 to 4 carbon atoms.
2. A polyisocyanate composition according to claim 1 in which the complex is a complex of titanium having a molar ratio of Ti to acetoacetate ester in the range 1 : 2 to 1 : 6.
3. A polyisocyanate composition according to claim 2 in which the molar ratio of Ti to acetoacetate ester is in the range 1 : 2.5 to 1 : 5.
4. A polyisocyanate composition according to any one of the preceding claims in which the acetoacetate ester is ethyl acetoacetate.
5. A polyisocyanate composition according to any one of the preceding claims in which the complex has been prepared from a titanium alkoxide having the general formula $M(OR)_4$ in which M is Ti and R is a substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group.
6. A polyisocyanate composition according to claim 5 in which R contains up to 6 carbon atoms.
7. A polyisocyanate composition according to claim 6 in which R contains up to 4 carbon atoms.
8. A polyisocyanate composition according to any one of claims 1 to 7 in which the complex has been prepared from a condensed titanium alkoxide having the general formula $RO[M(OR)_2O]_xR$ in which M is Ti and x is an integer and R is a substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group.

9. A polyisocyanate composition according to claim 8 in which the average value of x is in the range 2 to 16.
10. A polyisocyanate composition according to any one of the preceding claims in which the complex is prepared from an alkoxide or condensed alkoxide and displaced alcohol is removed.
11. A polyisocyanate composition according to any one of the preceding claims in which the complex is present in an amount in the range 0.03 to 1 % by weight based on the polyisocyanate.
12. A polyisocyanate composition according to claim 11 in which the amount of complex is in the range 0.05 to 0.5 % by weight based on the polyisocyanate.
13. A polyisocyanate composition according to any one of the preceding claims in which the polyisocyanate is diphenylmethane diisocyanate or a mixture of methylene bridged polyphenyl polyisocyanates.
14. A polyisocyanate composition according to any one of the preceding claims additionally comprising a diluent.
15. A polyisocyanate composition according to claim 14 in which the diluent is a phthalate, an aliphatic carboxylate, a fatty acid ester, linseed oil or soybean oil.
16. A polyisocyanate composition according to claim 15 in which the diluent is present in an amount in the range 1 to 40 parts by weight per 100 parts by weight of polyisocyanate.
17. A polyisocyanate composition according to any one of the preceding claims additionally comprising a formaldehyde condensate adhesive resin.
18. A polyisocyanate composition according to claim 17 in which the formaldehyde condensate adhesive resin is present in an amount in the range 1 to 40 parts by weight per 100 parts by weight of polyisocyanate.

19. A polyisocyanate composition according to claim 18 in which the formaldehyde condensate adhesive resin is present in an amount in the range 1 to 20 parts by weight per 100 parts by weight of polyisocyanate.
20. A process for binding lignocellulosic material comprising the steps of
- 5 a) bringing lignocellulosic material into contact with a polyisocyanate composition according to any one of the preceding claims and
- b) subsequently allowing said material to bind.
21. A process according to claim 20 in which the polyisocyanate composition is brought into contact with the lignocellulosic material and the combination thereby formed is
- 10 hot-pressed between metal plates at a temperature in the range 140° C to 270° C and a specific pressure in the range 2 to 6 MPa.
22. A process according to claim 20 or 21 in which the polyisocyanate composition is applied in such an amount as to give a weight ratio of polyisocyanate to lignocellulosic material in the range 0.1 : 99.9 to 20 : 80.
- 15 23. Use of a Titanium complex as defined in claim 1 for accelerating the binding of lignocellulosic materials.

ABSTRACT

Use of Titanium complex in a polyisocyanate composition comprising a titanium complex consisting of titanium and an acetoacetate ester in which the molar ratio of Ti to acetoacetate ester is in the range 1:2 and 1:8 and said acetoacetate ester is an ester of alcohol

5 containing 1 to 4 carbon atoms for accelerating the binding of lignocellulosic materials.

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FOR UTILITY/DESIGN
CIP/PCT NATIONAL/PLANT
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DECLARATIONS

RULE 63 (37 C.F.R. 1.63)
DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PW
FORM

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the INVENTION ENTITLED POLYISOCYANATE COMPOSITIONS FOR FAST CURE

the specification of which (CHECK applicable BOX(ES))

X A. ☐ is attached hereto.

BOX(ES) → B. ☐ was filed on

as U.S. Application No. /

→ C. ☒ was filed as PCT International Application No. PCT/ EP00/06057 on 29 June 2000

and (if applicable to U.S. or PCT application) was amended on

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56. Except as noted below, I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International Application which designated at least one other country than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate, or PCT International Application, filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing date of this application.

PRIOR FOREIGN APPLICATION(S)

Number
99114601.0

Country
EP

Day/MONTH/Year Filed
26 July 1999

Date first Laid-
open or Published

Date Patented
or Granted

Priority NOT Claimed

If more prior foreign applications, X box at bottom and continue on attached page.

Except as noted below, I hereby claim domestic priority benefit under 35 U.S.C. 119(e) or 120 and/or 365(c) of the indicated United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application:

PRIOR U.S. PROVISIONAL, NONPROVISIONAL AND/OR PCT APPLICATION(S)

Application No. (series code/serial no.)

Day/MONTH/Year Filed

Status
pending, abandoned, patented

Priority NOT Claimed

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Pillsbury Winthrop LLP, Intellectual Property Group, telephone number (703) 905-2000 (to whom all communications are to be directed), and persons of that firm who are associated with USPTO Customer No. 909 (see below label) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete from that Customer No. names of persons no longer with their firm, to add new persons of their firm to that Customer No., and to act and rely on instructions from and communicate directly with the person/assignee/attorney/firm/ organization who/which first sends/sent this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above Firm and/or an attorney of that Firm in writing to the contrary.

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